



# Linearity Limits for Several Trace Metals Currently Determined by Electrothermal Atomic Absorption Spectrometry

## Application Note

Atomic Absorption

### Authors

Michel Hoenig and  
Paul Van Hoeyweghen  
Institut de Recherches Chimiques  
Ministere de l'Agriculture  
Museumlaan 5 – 1980 Tervuren  
Belgium

### Introduction

Atomic absorption spectrometry is a comparative method since a linear relationship exists between the concentration of free atoms in the optical path and their absorbance. In practice, deviation from the Beer-Lambert law is often observed, especially at higher absorbance values. This can be caused by several factors:

- a. Occasionally by a hyperfine structure of the spectral line. Many spectral lines have this kind of fine structure due to isotope shifts and nuclear spin.
- b. Most frequently by light which cannot be absorbed [1,2]. This can be stray light in the accepted sense, but more usually it is background radiation from the light source.

Quantitative absorption of incident light by atoms can only take place if the half-width of the emission line from the radiation source is considerably smaller than the half-width of the absorption line.

If this is not the case, the absorption profile will be flanked on both sides by non-absorbable, residual radiation which acts as radiation background.

- c. The occurrence of calibration curvature can be considerably influenced by the total width of the omitted lines (from the filler gas, cathode material, or with analytes that have so many lines in their emission spectra that the resonance line cannot be separated from other non-absorbable lines).
- d. Electrothermal atomic absorption spectrometry can produce very fast absorbance pulses, especially for volatile elements such as cadmium and zinc. This necessitates fast responses in the detection system. With earlier spectrometers, the slow response caused by high time constants and insufficient sampling of the absorbance signal could also influence the initial linearity of the calibration graph [3].



**Agilent Technologies**

When a particular sample is analyzed for the first time, it is good practice to compare the method of standard additions with the direct calibration procedure. The standard additions method assumes that the added analyte will be affected by non-spectral interference in the same way and to the same extent as the analyte in the sample.

If the slopes of the two plots are substantially the same it can be assumed that the sample can be analyzed without matrix effect by using direct calibration against simple aqueous standards. If, however, the slopes are not the same it will be necessary to use the standard additions method. As a general rule, the standard additions scheme used must provide substantially linear calibration since accurate results cannot be obtained from a non-linear calibration plot.

With this in mind, we have carried out studies to establish the linear working range for several elements currently determined by electrothermal atomic absorption spectrometry. Note, however, that the values specified here must be regarded with caution. They were obtained with a particular instrumental system and with hollow cathode lamps, graphite tubes and platforms of various ages. Obviously, the limits obtained may vary from one set of equipment to another, although the general tendency should remain the same.

## Experimental

All work was performed on an Agilent SpectrAA-10 spectrometer equipped with an Agilent GTA-96 graphite tube atomizer and programmable sample dispenser. Pyrolytically coated graphite tubes and pyrolytic platforms were used throughout.

The age of the hollow cathode lamps used in the study varied from new to 10 years old (age in years of normal use is shown in brackets):

Al (4); As (1); Cd (2); Co (5); Cr (5); Cu (new); Fe (10); Ni (6); Mn (8); Mo (3); Pb (2); Sb (4); Se (4); Ti (new); Tl (4); V (8). They were operated at currents and slit settings recommended by the manufacturer.

Details of general furnace programs are given in Table 1. Atomization temperatures (steps 5 and 6 for wall; steps 4 and 5 for platform) were specific for each element, hence the notation "var" in Table 1. All measurements were performed in the peak height mode.

The aqueous standards were prepared in 2% nitric acid from commercial standard solutions (Titrisol Merck).

Table 1. *Electrothermal Programs Used for Studies in Simple Acid Medium.*

A: Tube wall atomization

**Injection temperature: 40°C.**

Step	Temperature (°C)	Time (sec)	Gas flow (L/min)	Read
1	100	30	3	—
2	300	5	3	—
3	300	5	3	—
4	300	2	0	—
5	var	max heat rate	0	Yes
6	var	2	0	Yes
7	40	var	3	—

B: Platform atomization

**Injection temperature: 100°C**

Step	Temperature (°C)	Time (sec)	Gas flow (L/min)	Read
1	300	30	3	—
2	300	5	3	—
3	300	2	0	—
4	var	max heat rate	0	Yes
5	var	2	0	Yes
6	100	var	3	—

## Results

The experimental results are presented in Table 2 and Table 3. For each element studied, characteristic mass represents the amount of analyte (pg) that produces 0.0044 absorbance. The elements of high and medium volatility were tested using both wall and platform atomization.

Linearity limits are expressed in absorbance units and corresponding mass. The logarithm of the linearity limit to characteristic mass ratio gives the number of linear orders of magnitude attained. It must be noted that cadmium (one of the most volatile elements determined by EAAS) shows a very high linearity limit. This confirms that the detection system is fast enough. The premature curvature for some elements is thus due to other phenomena described in the introduction.

The most affected element is nickel; the spectral band width of 0.2 nm is probably too broad. It can be assumed that the use of a narrower slit (0.1 for example) will improve the linearity for nickel and other elements producing a rich emission spectrum.

Thallium also exhibits premature curvature compared to other elements of similar volatility such as lead and antimony. We have no valid explanation for this particular case, but it is probably due to the particular atomization mechanism of thallium. It should be noted that the addition of ascorbic acid as a modifier considerably improves calibration linearity.

For other analytes, the study was performed without modifiers. It is probable that their use will influence linearity for other elements.

Table 2: Atomization Off Tube Wall

Element and wavelength		Char. mass m <sub>0</sub>	Linearity limit (Abs)	Linearity limit (pg)	L*	log L
Al	309.3	6.6	0.50	750	125	2.10
As	193.7	8.8	0.40	800	95	1.98
Cd	228.8	0.26	0.60	36	129	2.11
Co	240.7	2.9	0.20	130	45	1.65
Cr	357.9	0.82	0.35	65	78	1.89
Cu	324.7	1.6	0.30	110	69	1.84
Fe	248.3	0.88	0.30	60	67	1.83
Mn	279.5	1.0	0.52	120	133	2.12
Mo	313.3	2.0	0.45	200	111	2.05
Ni	232.0	6.6	0.12	180	28	1.45
Pb	217.0	2.2	0.30	150	65	1.81
Sb	217.6	11.7	0.30	800	73	1.86
Se	196.0	13.2	0.20	600	50	1.70
Ti	364.3	31.7	0.50	3600	113	2.05
Tl	276.8	6.6	0.20	300	44	1.64
V	318.5	13.2	0.30	900	69	1.84

\* L = Linearity limit (pg) characteristic mass

Table 3: Atomization Off the Platform

Element and wavelength		Char. mass m <sub>o</sub>	Linearity limit (Abs)	Linearity limit (pg)	L*	log L
Al	309.3	6.2	0.50	700	140	2.15
As	193.7	7.5	0.35	600	80	1.90
Cd	228.8	0.26	0.45	27	112	2.05
Cu	324.7	4.3	0.45	440	102	2.01
Mn	279.5	1.2	0.55	150	125	2.10
Pb	217.0	2.2	0.30	150	65	1.81
Sb	217.6	10.8	0.45	1100	110	2.04
Se	196.0	13.2	0.40	1200	100	2.00
Tl	276.8	5.9	0.15	200	31	1.49
	(i)	5.9	0.30	400	62	1.79

(i) with ascorbic acid as modifier

\* L = Linearity limit (pg) characteristic mass

## References

1. A. C. Menzies, Anal. Chem. 32, 898 (1960).
2. H. Prugger, Optik 21, 320 (1964).
3. M. Hoenig, Spectrochim. Acta 37B, 929 (1982).

## For More Information

For more information on our products and services, visit our Web site at [www.agilent.com/chem](http://www.agilent.com/chem)

[www.agilent.com/chem](http://www.agilent.com/chem)

Agilent shall not be liable for errors contained herein or for incidental or consequential damages in connection with the furnishing, performance, or use of this material.

Information, descriptions, and specifications in this publication are subject to change without notice.

© Agilent Technologies, Inc., 1987  
Printed in the USA  
November 1, 2010  
AA074



**Agilent Technologies**